Synopsis

Design and Applications of Bile-salt/Lanthanide based Hydrogels

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Chapter 1: Introduction to the luminescent properties of lanthanides

Luminescence properties of trivalent lanthanides have been explored extensively over the past few decades owing to their unique properties. Lanthanides emission is known to be due to intra-configurational f-f transitions. Because the partially filled 4f shell is well shielded from its environment by the closed $5s^2$ and $5p^6$ shells, the ligands in the first and second coordination sphere perturb the electronic configurations of the trivalent lanthanide ions only to a very limited extent. This leads to interesting properties such as long lifetimes, sharp line-like emissions etc. which in turn make lanthanides very attractive choice for commercial optical applications.

Despite this, the scope of applications remained limited because of the low molar extinction coefficient values of the forbidden lanthanide f-f transitions. However, this problem has been successfully addressed by complexing the lanthanide ion with suitable ligands which can sensitize it resulting in a significant increase in the emission intensity (so called “antenna effect”). The strategy worked very well and resulted in widespread applications of lanthanides form biology to optoelectronics. This chapter discusses elementary ideas regarding the mechanism of sensitization and relevant examples that traces various applications of such lanthanide complexes from the current literature.

Chapter 2: A self-assembled Europium Cholate hydrogel: a novel approach towards lanthanide sensitization

Luminescent lanthanides can be of great value in a number of possible applications but their scope is limited by their intrinsic low molar absorptivities. Though this problem can be circumvented by complexing the lanthanide ion with suitable chelating ligands to improve the luminescence properties drastically, the design of such systems often involves meticulous planning and laborious synthetic steps to obtain a ligand suitable for the job. It is therefore desirable to have a simpler version of a sensitizing system that does not require the complexities of a chelating ligand but can sensitize trivalent lanthanides with comparable efficiency.

It was observed in our group that divalent metal ions (Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} *etc.*) form hydrogels on addition of sodium cholate. We extended to obtain hydrogels of trivalent lanthanides. Furthermore, when the gel was doped with pyrene, a ten-fold increase in the intensity of Eu(III) emission was observed (Fig 2). Thus we established a unique way to sensitize lanthanides in a hydrogel media by non-coordinating chromophores. The approach was completely modular in nature and avoids any laborious synthesis. We also tried other derivatives of pyrene as sensitizers and found that 1-pyreneboronic acid also caused similar sensitization of Eu(III).

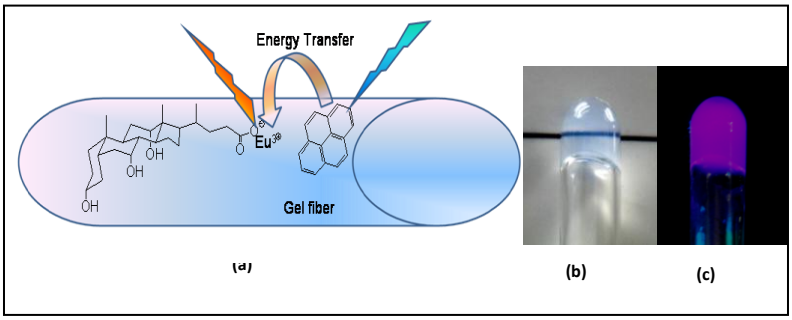

Fig 2. (a) Schematic representation of the sensitization process (the arrangement of molecules in the gel fiber is arbitrary). Eu-cholate (5 mM/15 mM) gel (a) normal light and (b) 354 nm UV excitation in the presence of 6 μM pyrene

Further studies revealed, that 2,3-dihydroxynapthalene (DHN) can sensitize Tb(III) in a similar hydrogel. We also demonstrated Tb(III) to Eu(III) energy transfer process occurring in the gel when doped with DHN. This allowed us to achieve a hydrogel system with tunable luminescence properties (by varying relative ratios of Tb(III) and Eu(III)). When the effect of divalent metal ions on such energy transfer processes were explored, it was observed that the luminescence from the composite gel of Tb(III)/ Eu(III) is tunable by Zn(II) and through proper manipulation of concentrations one can obtain white light emitting gel (Fig 3).

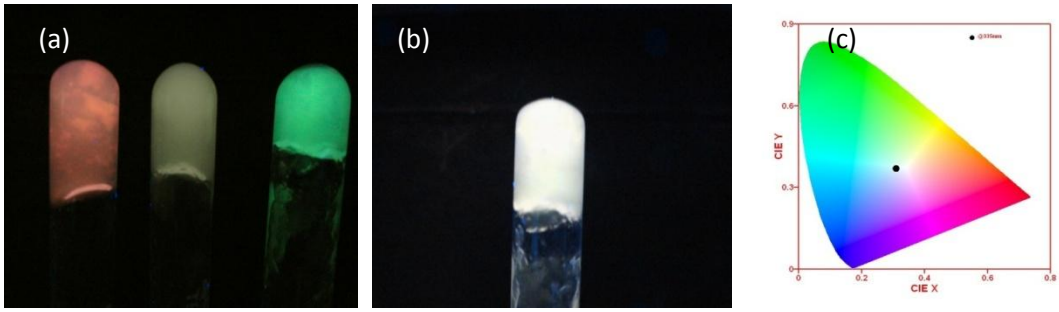

Fig 3. Effect of Zn(II) (from left to right 0 mM, 2.8 mM, 11.3 mM) on Tb^{3+} (4.5 mM)/Eu^{3+} (0.11mM)/ sodium cholate (13.6 mM) gels. b) Tb/Eu/Zn-cholate gel (Tb^{3+} (4.4 mM), Eu^{3+} (0.11 mM), Zn^{2+} (7.4 mM), NaC (13.6 mM, DHN 0.2 mM) under 365 nm UV lamp (c) CIE 1931 diagram depicting the luminescence as white (black spot).

Chapter 3. A "Pro-Sensitizer" based Sensing of Enzymes using Tb(III) Luminescence in a Hydrogel matrix

This chapter descirbes design and realisation of a sensor system based on Tb(III) luminescnece for the detection of enzymes. The idea involved synthesizing a covalently modified DHN molecule by attaching appropriate enzyme cleavable units. We coined the term ***"pro-sensitizer"*** to describe the modified molecule which would not sensitize Tb(III) in the gel matrix but when proper enzymes are applied the free form of DHN would be released triggering a luminescence response from Tb(III). This would enable us to monitor the acitivities of the particular enzyme by examining the luminescence intensity enhancement with time (Fig 4)

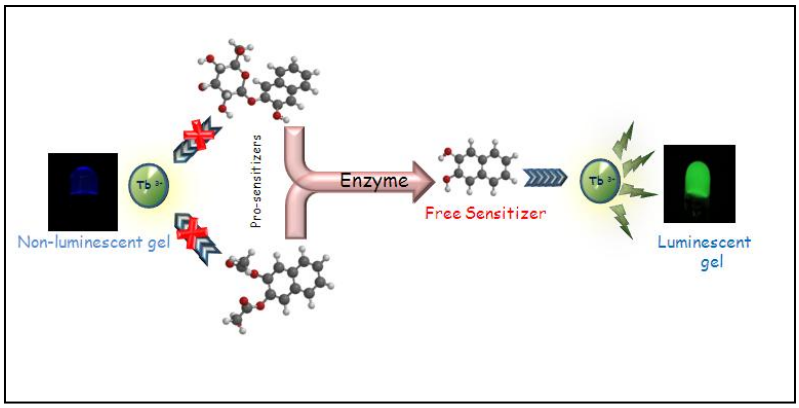

Fig 4. A "pro-sensitizer" based approach to detect different types of enzymes in a hydrogel matrix through Tb(III) luminescence.

We applied the idea to develop a novel luminogenic gel probe for inexpensive and rapid detection of three different hydrolases, lipase, β–glucosidase and α-chymotrypsin. The corresponding ***"pro-sensitizer"*** for each enzyme were synthesized (Fig 5)**.**The sensing technique depends on the gel matrix to provide the nessesary platform for lanthanide sensitization. Thereofore, it enjoys an edge over the contemporary techniques that typically involve specially designed and synthesized multidentate chelating ligands for this purpose. We also determined important kinetic parameters of all the enzymes, thus enabling us to have a better insight into the activity of the enzymes in the hydrogel matrix.

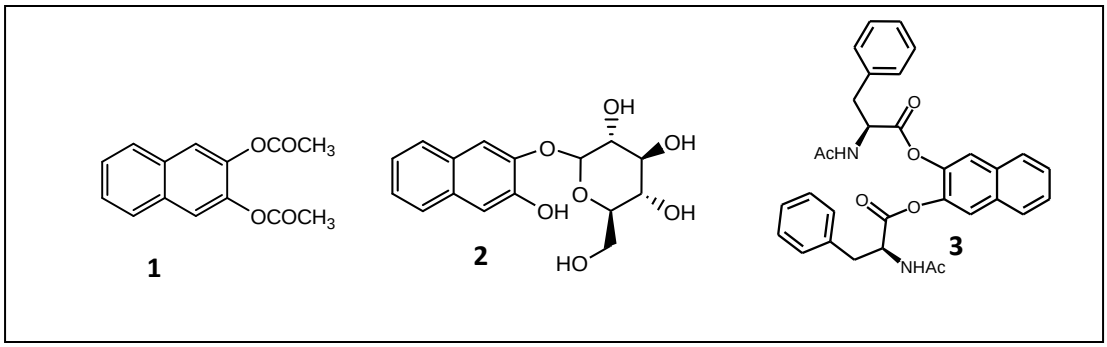

Fig 4. Pro-sensitizers molecules for (**1**) lipase, (**2**) β-glucosidase and (**3**) α-chymotrypsin

Chapter 4. A novel approach towards templated synthesis of lanthanide trifluoride nanoparticles

Nanomaterials with excellent optical properties have been of special interest. Lanthanide derived nanoparticles, owing to their unique physical properties, provide an excellent choice for applications such as biolabels, lasers, optical amplifiers, and optical-display phosphors. Several types of lanthanide nanoparticles or nanocrystals are reported in the literature such as Nd_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, and Y_2O_3. Among them lanthanide fluoride nanoparticles have emerged as the best choice because of their low phonon energy, and thus minimum quenching of emissive Ln^{3+} ions thereby allowing maximum efficiency for several optical applications. In previous literature precedence, LnF_3 nanoparticles were typically synthesized following conventional approaches which necessitate use of high temperatures, high pressures (hydrothermal techniques) and capping ligands. In this chapter, we demonstrated a simpler synthesis of LnF_3 nanoparticles at ambient temperatures without the requirement of added capping agents. The room temperature synthesis of LnF_3 was unprecedented and was achieved simply by diffusing NaF solution through the hydrogels of corresponding Ln-cholate gels. The nanoparticles were characterized by transmission electron microscopy (TEM) and by powder XRD analysis which established the presence of very small (3-4 nm) nanoparticles mono-dispersed uniformly over the the gel matrix (Fig 6). The LnF_3 containing xerogels of Tb(III) and Eu(III) cholate gels were also shown to be highly emissive.

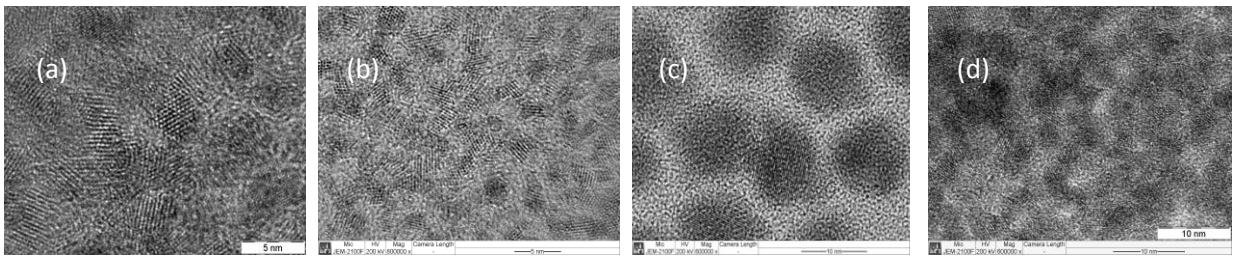

Fig 6. HRTEM images of a) TbF_3, b) GdF_3, c) NdF_3 and d) DyF_3 in their corresponding gel media.